MAPLE SIRUP. IV. EFFECT OF HEATING SIRUPS UNDER CONDITIONS OF HIGH TEMPERATURE AND LOW WATER CONTENT: SOME PHYSICAL AND CHEMICAL CHANGES

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In previous publications *(3, 5)* and in a patent *(6)*, it was stated that additional maple flavor and increased color can be developed in a commercial maple sirup by heating it at the elevated boiling temperatures obtained by atmospheric evaporation of the sirup to a sufficiently high solids content. This observation was based on the following experimental facts: (1) sirups of normal flavor and color are made from normal sap by atmospheric evaporation to a solids content of 65-67%; (2) concentration of normal sap by freeze drying produces a colorless and flavorless sirup, proving that normal sap is devoid of flavor and color; (3) maple flavor and the usual amber color can be produced in this colorless and flavorless sirup by heating at its boiling point. It was also shown that a high-flavored sirup produced by atmospheric evaporation of water from a normal sirup until the solids content reached 85-90% and holding at the elevated boiling point of the more concentrated sirup, had much less caramel and other off-flavors than was produced by heating sirups in an autoclave for identical times and temperatures where the solids were kept at 65.5% *(5)*. No data on quantitative changes in the heated sirup were given, nor were any data given showing the effect of time and temperature on the flavor and color of the heated sirup.

The data presented in this paper indicate some of the changes that take place under the different heating conditions.

MATERIALS, METHODS, AND PROCEDURE

Materials. The sirups were of two commercial table grades, Fancy (U. S., New York, or Vermont Grade) and New York Grade No. 3 (Vermont Grade C). These grades were chosen because they represent the extremes of the commercially available sirup. Previous work demonstrated that data for intermediate grades of sirup will fall between the data obtained with these two sirups.

Equipment. The sirups were heated in small, stainless steel, steam kettles which were two-thirds jacketed and which could be operated with steam pressures up to 40 p.s.i. One gallon of sirup more than filled the jacketed portion of this small kettle. An electric stirrer (600 r.p.m.) was used to keep the thickened sirup in motion and prevent super-heating at the surfaces of the kettle. To minimize further evaporation, a tight-fitting, stainless steel lid was placed on the kettle when the desired boiling point was reached.

Methods and procedure. The samples of sirup were defecated with lead and deleaded with potassium oxalate. Schoorl's method *(1)* was used to determine free invert sugar and reducing sugars after inversion with hydrochloric acid at room temperature.

Color was evaluated in terms of light-absorption measurements at 450 mμ in the General Electric recording spectrophotometer, with water as a blank, and a solution

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diluted to give observed absorbance (optical density) in the range 0.2 to 0.8. From this measurement, a color index was calculated as the absorbance at 450 mμ for a 1-cm. depth of solution having 86.3 gms. of solids per 100 ml. of solution.

This color index = $A_{1cm.}^{86.3\%} = A_{450}$ (86.3/bc), where A_{450} is the observed absorbance at 450 mμ, b is the depth of the solution in centimeters (1 cm. in these experiments), and c is the grams of solids as sucrose per 100 ml. of solution, as determined on an Abbé refractometer. The maximum color indices of commercial sirups for the three U. S. Standard table grades are: U. S. AA (Light Amber), 0.506; U. S. A (Medium Amber), 0.900; and U. S. B (Dark Amber), 1.47.

Ultraviolet absorption measurements were made on a Cary recording spectrophotometer, with the same solutions against water as a blank. From these data, absorptivities were calculated.

Hydrogen ion concentrations (pH) were determined with glass electrodes on aliquots of the diluted samples used in the spectrophotometric studies.

One gallon of the sirup was placed in the steam kettle and heated with 35 p.s.i. steam, bringing the sirup to boiling as rapidly as possible. Vigorous boiling was continued to remove sufficient water to elevate the boiling point to the desired temperature. The kettle lid was set in place and the steam pressure reduced sufficiently to hold the concentrated sirup at a simmering boil at the temperature being investigated. This temperature was maintained constantly throughout the heating period. When samples were removed for analysis, however, the boiling equilibrium was often upset, resulting in an increase of about 2°F. for a short period until the boiling equilibrium could be re-established by addition of a small amount of water.

A sample of the original sirup was analyzed for (a) pH, (b) absorption at 450 mμ, (c) general absorption in the ultraviolet region of the spectrum, (d) invert sugar, and (e) reducing sugars after inversion by the methods given above. Samples of the cooking sirup were taken when the sirup first reached the temperature being studied, which was designated as zero time. Other samples were taken at half-hour intervals until the material was no longer usable because of off-flavors. Each sample of heated sirup was adjusted to the same refractive index (solids content) as that of the original sirup by the addition of distilled water so that they would be on a comparable basis. If the boiling point began to rise because of incomplete reflux, distilled water was added to the sirup to return the boiling point to that being studied. The temperatures used were 235°, 244°, and 252°F. for the two grades of sirup. The approximate water content of the sirups at these boiling temperatures were 20, 15, and 10%, respectively *(4)*.

RESULTS AND DISCUSSION

Table 1 gives data on changes in the pH, color index at 450 mμ, the percentage of invert sugar, and flavor that occurred in the two grades of sirup heated at the three temperatures for the periods indicated. Flavor level was determined by dilution of the sample with colorless and flavorless cane sugar sirup (having a refractive index the same as the original maple sirup) required to yield a flavor equivalent to that of the original maple sirup. Thus, a 1 + 3 dilution means that 1 volume of the sample was diluted with 3 volumes of cane sugar sirup and indicates a fourfold increase in flavor over the original sirup or a flavor enhancement of 4. A small group of conditioned testers was used to determine flavor levels.

Figure 1 shows the effect on the invert sugar content of time of cooking at each of the three temperatures. Figure 2 shows the effect on the color, in terms of absorption at 450 mμ, of time of cooking. Figure 3 shows the ultraviolet absorption spectrum obtained with the No. 3 sirup before and after it was cooked for 6 hours at 252°F.

Prolonged heating of the Fancy grade sirup resulted in a decrease in pH, amounting to approximately 1.5 units. The same treatment of No. 3 sirup lowered the pH less than 0.2 unit. These changes in pH are signifi-

TABLE 1

Analyses of maple sirups heated for different times at various temperatures above the normal boiling temperature

Heating time	Fancy grade				No. 3 grade			
	pH	Invert sugar content	Color index $A^{\frac{66.3\%}{1\,cm.}}$	Flavor enhancement factor[1]	pH	Invert sugar content	Color index $A^{\frac{66.3\%}{1\,cm.}}$	Flavor enhancement factor[1]
Boiling temperature, 235°F.								
Hours		%				%		
Orig.	7.0	0.31	0.30		6.7	1.74	1.91	
0	7.0	.31	.39		6.6	1.81	2.23	
0.5	7.0	.34	.52		6.7	1.96	2.43	
1.0	6.8	.45	.62		6.6	2.16	2.81	
1.5	6.7	.53	.76		6.6	2.46	3.06	
2.0	6.6	.61	.89	3	6.6	2.80	3.34	
2.5	6.4	.69	1.03	4	6.6	3.20	3.71	
3.0	6.8	.82	1.16	5	6.6	3.64	3.99	
3.5	6.1	.94	1.32	6	6.6	4.32	4.28	
4.0	6.0	1.08	1.46		6.6	4.99	4.63	
5.0	5.9	1.43	1.87		6.6	6.77	5.37	
6.0	5.8	2.16	2.28		6.6	9.05	6.11	3
Boiling temperature, 244°F.								
Orig.	7.0	0.31	0.30		6.7	1.74	1.91	
0	6.7	.33	.44		6.6	1.88	2.49	
0.5	6.7	.41	.61		6.6	2.11	2.98	
1.0	6.5	.54	.82	3	6.6	2.42	3.40	
1.5	6.3	.72	1.02	3	6.6	2.94	3.89	
2.0	5.7	.92	1.25	4	6.6	3.35	4.31	
2.5	5.6	1.19	1.51	5	6.6	4.28	4.79	
3.0	5.4	1.56	1.78		6.6	5.21	5.27	
3.5	5.5	2.04	2.09		6.6	6.32	5.87	
4.0	5.5	2.59	2.43		6.6	7.72	6.43	3
5.0	5.4	4.15	3.33		6.5	10.95	7.72	4
6.0	5.4	6.14	4.27		6.5	15.50	9.25	6
Boiling temperature, 252°F.								
Orig.	7.0	0.31	0.30		6.7	1.74	1.91	
0	6.6	.46	.69		6.9	2.10	2.89	
0.5	6.1	.66	1.01	3	6.8	2.50	3.55	
1.0	6.0	.95	1.36	4	6.7	3.17	4.18	
1.5	5.7	1.31	1.74	5	6.7	4.11	4.86	
2.0	5.4	1.93	2.19	7	6.6	5.31	5.58	
2.5	5.5	2.59	2.67		6.6	7.17	6.39	3
3.0	5.4	3.36	3.18		6.6	9.15	7.26	4
3.5	5.4	4.40	3.94		6.6	11.01	8.27	5
4.0	5.0	5.97	4.62		6.6	14.29	9.58	
5.0	5.0	9.21	6.25		6.6	21.52	12.95	
6.0	5.0	13.81	8.45		6.6	31.45	17.61	

[1]Flavor enhancement factor of the high-flavored sirup is the ratio of the volume of a blend (1 part of high-flavored sirup + x parts of cane sugar sirup) to one volume of original sirup, both of identical flavor level.

cant because several runs on different sirups gave substantially the same results. The cause of these changes is not fully known. Paper chromatograms of the organic acids from the heated sirups indicated that no change occurred in the number of acids present. However, the color materials, which are acidic and do not migrate to any extent on paper chromato-

grams, did show a relatively large increase. The increase in these acidic substances was detected during the isolation of the organic acid fraction by means of ion-exchange. The amount of anion exchange material required to prevent break-through for a given weight of sample was much larger for the cooked, colored sample than for the uncooked sample. This increase in acidic substances might account for the decrease in pH.

Invert sugar was produced by hydrolysis of the sucrose at all the temperatures studied. The rate of its production was highest at 252°F. and in the No. 3 sirup (Figure 1). Analysis for total reducing sugars after inversion showed that but little sugar was destroyed in the heat-treated sirups except in the No. 3 sirup when heated at the highest temperature (252°F.), in which case a 2% decrease in total sugars was observed. In all cases, the increase in invert sugar was accompanied by a corresponding loss of sucrose, indicating that the amount of sugar involved in the darkening process, either by caramelization or by browning, was small and that the tinctorial power of the coloring materials was high. The rate of invert sugar production approximated a log function.

As indicated in Figure 2, the rate of color development increased as the time of heating increased. The similarity in the shapes of the curves for invert sugar formation and color formation suggests a correlation between these two variables. An evaluation of the data, however, indicates that no direct or simple relationship exists. This fact suggests that the production of color may be related to the formation of some intermediate products from the thermal decomposition of the reducing sugars, and possibly that the reaction of these sugar decomposition products with

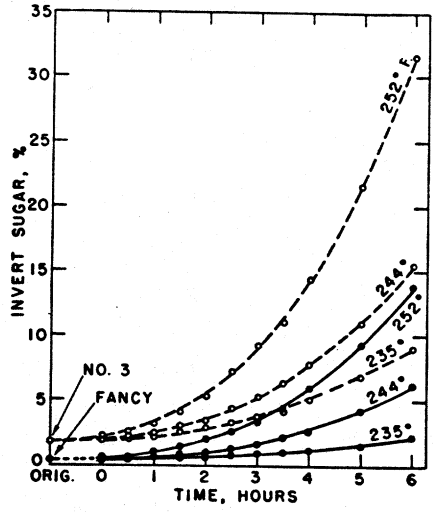

Figure 1. Development of invert sugar in two commercial grades of maple sirup heated at 235°, 244°, and 252°F. for different periods of time under atmospheric pressure.

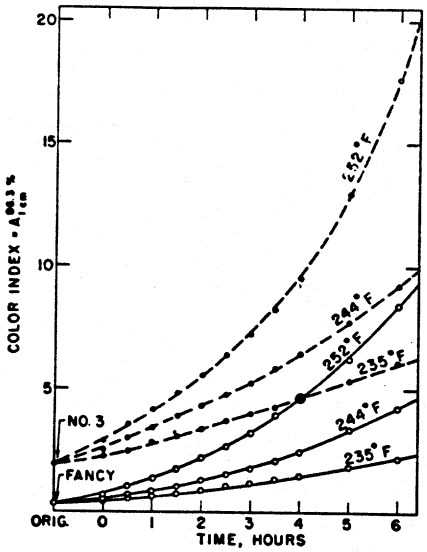

Figure 2. Color index at 450 mμ of two commercial grades of maple sirup heated at 235°, 244°, and 252°F. for different periods of time under atmospheric pressure.

other sirup constituents, as in a browning reaction *(2, 8)*, is responsible for the developed color.

Both grades of sirup darkened during the heating, but the rate of color development, as measured by absorption at 450 mμ was greater at the higher boiling temperatures. It was also greater with the darker grade of sirup than with the lighter grade. Paradoxically, less time was required for a fourfold increase in color index for the Fancy sirup than for the No. 3 sirup (Table 1). Since Fancy sirup is light in color (low color index), the amount of the color bodies that must be produced by the high-flavored process to give a fourfold increase is less than that required for a fourfold increase of color bodies in a No. 3 sirup. However, to develop the same color in a Fancy sirup as in a No. 3 sirup heated for a specified time, the lighter (Fancy) sirup would require a much longer heating treatment.

Interpretation of the ultraviolet absorption spectra for these samples (Figure 3) indicated the production of a conjugated unsaturated material,

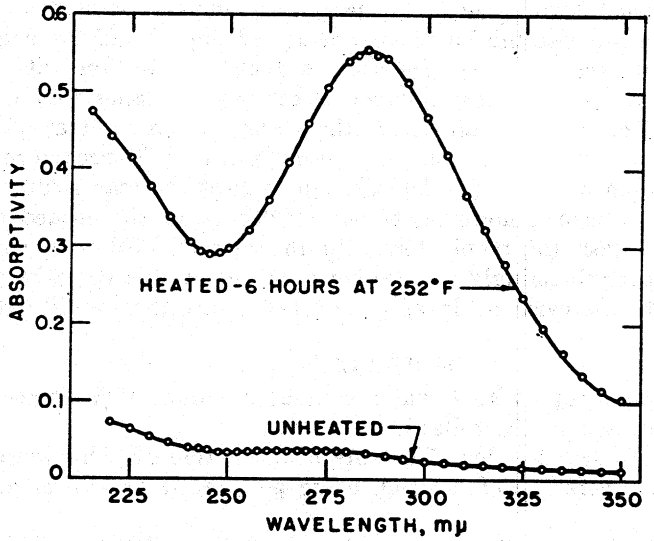

Figure 3. Ultraviolet absorption spectrum of maple sirup (commercial grade No. 3) before and after heating the sirup for 6 hours at 252°F. under atmospheric pressure. Absorptivity is equal to absorbance referred to unit cell length (1 cm.) and unit solids concentration (1 gm./liter).

with an absorption maximum at 285 mμ, the production rate of which followed closely the rate of color development as measured by absorption at 450 mμ. The wave-length of the absorption maximum suggested that the material might be 5-hydroxymethyl-2-furfuraldehyde. Extraction with ethyl acetate of the sirup cooked for 6 hours produced an extract that was insoluble in water *(8)*. The 2,4-dinitrophenylhydrazone derivative of this extract was prepared. This derivative could not be purified by recrystallization from hydrous ethanol solutions and it was necessary to affect purification by chromatographic adsorption on cellulose powder, with ether as

the solvent. An ether solution of the impure hydrazone obtained after recrystallization was placed on a cellulose powder column,[2] and elution was carried out with anhydrous ether. The impurities were preferentially adsorbed, and the derivative was passed through the column in the effluent, from which it was crystallized by slow evaporation of the solvent. Both direct and mixed melting points (197-199° C., corrected) showed that these crystals were identical with those of the derivative made from pure 5-hydroxymethyl-2-furfuraldehyde. Based on a molar absorptivity (a_m) of 16,500 *(7)*, the maximum quantity of 5-hydroxymethyl-2-furfuraldehyde which could be present was 0.4%. It should not be assumed, however, that the hydroxymethylfurfural was responsible for the darkening, since it might have been an end-product of the decomposition of some of the sugars and not an intermediate that reacted to form the coloring material in question. Further study to determine the identity of the coloring materials and to obtain a knowledge of their source is necessary for complete understanding of formation of color in maple sirup.

The increase in maple flavor paralleled the increase in color up to the point where caramel flavor completely masked this more delicate flavor. In general, the data indicate this interdependency (Table 1). If the original color of a sample was darkened fourfold, a fourfold dilution with cane sirup produced a blend having a flavor closely approaching that of the original sirup. This is important, since the absorption of light at 450 mμ can be used to determine the time necessary to reach a predetermined flavor level, eliminating the need for dilution with cane sugar sirup. This method is not applicable, however, if the off-flavors in the cooked sirup are sufficient to mask the maple flavor in the blend. Until the caramel flavor becomes overwhelmingly strong, however, blending with cane sirup appears to dilute the caramel flavor at a greater rate than it dilutes the maple flavor.

SUMMARY

Heating maple sirups with a water content of about 10% at elevated temperatures resulted in the following:

The sirups darkened in color. The rate of formation of color increased with time and temperature of heating, being greatest in the lower grades of sirup.

Development of maple flavor and color closely paralleled one another until the caramel and other off-flavors produced completely masked the more delicate maple flavor.

The content of invert sugar increased with time and temperature of heating. The rate of increase was greater in the darker sirup.

There was no simple relationship between the invert sugar content of the sirups and the rate of formation of color, suggesting that the role of intermediates should be more fully investigated.

The presence of 5-hydroxymethyl-2-furfuraldehyde was proved. The amount of this material increased with time and temperature of heating.

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[2] Cellulose powder was made by hammer milling Whatman Ashless Filter Paper Tablets. This was packed in a 1-cm. diameter tube from a suspension in ether. (Mention of commercial products does not imply endorsement by the Department of Agriculture over those of a similar nature not mentioned.)

This material may have no relationship to color but may be the end-product of another reaction.

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